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Pyramidal Structures: New Type of Cluster Compounds

著者（英）	Vladimir Yaroslavovitch LEE
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研究代表者

Ｌｅｅ　Ｖｌａｄｉｍｉｒ（Lee, Vladimir）

筑波大学・数理物質系・講師

研究者番号：９０３７５４１０

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研究成果の概要（和文）：ピラミダンとは有機化学における最も挑戦的な合成ターゲット分子の1つであるが、その顕著な重要性にもかかわらず、未だに合成されていない。 無置換母体ピラミダンはもちろん，その誘導体ですら単離，観測例はない。 本研究では、我々が以前に合成したシクロブタジエンジアニオンと典型元素ハロゲン化物との直接的な反応によってピラミダン誘導体を得るという全く新しい戦略を検討した。 高周期14族元素を頂点に有するピラミダンおよび高周期１５族元素のカチオン等電子体の合成に成功した．すべての新たに合成したピラミダンはX線結晶構造解析によりその分子構造を明らかにした．

研究成果の概要（英文）：Pyramidanes are among the most challenging synthetic targets for organic chemistry, which are still eluded their synthetic realization despite their evident interest and importance. Neither parent pyramidane C[C4H4] nor its derivatives have ever been isolated and characterized. In the current project, we proposed and developed totally new synthetic strategy for the preparation of such elusive species by the straightforward reaction of the readily available cyclobutadiene dianion derivatives (developed in our group) with the main group elements halides. Using this simple approach, we succeeded in the synthesis of a whole series of the neural group 14 element pyramidanes and their isoelectronic cationic counterparts featuring heavier group 15 element at the top of the square pyramid. All newly isolated pyramidanes were undoubtedly structurally characterized.

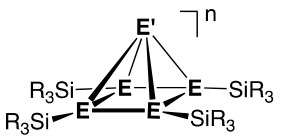
研究分野：　有機化学

キーワード：　cluster　pyramidane　housene　cyclobutadiene dianion　group 14 element　group 15 element

１．研究開始当初の背景

Pyramidal compounds (square pyramids, pentagonal pyramids, etc.) with their non-classical inverted geometry and hypercoordination at the apex are among the most fascinating organic chemistry targets, that challenge such fundamental textbook postulates as tetrahedral configuration and tetravalency of the sp^3-carbon atoms. This is further reinforced by the very usual non-classical bonding mode between the apex and base that cannot be adequately described by the current bonding theory. However, despite such evident interest, pyramidanes still remained to be elusive species that have never been synthesized and isolated.

Using our extensive previous experience in the field of cyclic polyene ligand transition metal complexes, featuring "heavy" cyclobutadiene and "heavy" cyclopentadiene ligands, we attempted to develop a totally new approach for the synthesis of the main group element pyramidanes. Achieving this goal, we were planning to close the gap between the previously reported by us cyclobutadiene complexes of the *s*-block elements (alkali I alkaline earth metals) and *d*-block elements (transition metal complexes) by the synthesis of unprecedented cyclobutadiene complexes of the *p*-block elements, the so-called ***pyramidanes*** E′[$E_4(SiR_3)_4$] (E′ = group 13-15 element, E = C/Si/Ge) (Scheme 1).



Pyramidane

[n = –1, for E' = group 13
n = 0, for E' = group 14
n = +1, for E' = group 15]

Scheme 1

２．研究の目的

The final research goal of the current project is the development of the unprecedented pyramidal clusters of the main group elements. Following the synthesis of target pyramidanes, we were planning to investigate their non-classical bonding nature, structural and chemical properties, reactivity, and their potential application in the material science. Our synthetic strategy is based on the utilization of our readily available cyclobutadiene dianion derivatives $[(R_3Si)_4E_4]^{2-}\bullet 2Li^+$ (E = C, Si, Ge) [Lee et al.: *J. Am. Chem. Soc.* **2004**, *126*, 4758; *J. Am. Chem. Soc.* **2011**, *133*, 5103], that have already been used for preparation of a number of sandwich and half-sandwich complexes of transition metals [Lee et al.: *Angew. Chem. Int. Ed.* **2007**, *46*, 6596; *Chem. Soc. Rev.* **2008**, *37*, 1652]. At the key step, such cyclobutadiene dianion derivatives will be reacted with the main group halides RE′X_2 (E′ = group 13-15 element, X = halogen) forming the target pyramidal structures. Successful realization of the project purposes will have important impact from both academic and applied point of views. Thus pyramidanes, as the totally new class of cluster compounds, will be fundamentally interesting from the viewpoint of their non-classical structures, and unusual physic-chemical and chemical properties. On the other hand, pyramidal structures can serve as the convenient precursors for novel transition metal complexes having cyclobutadiene ligand. The latter compounds are of great interest as the precursors for new advanced materials for catalysis, alkene polymerization, nonlinear optical materials, molecular magnets, luminescent and fluorescent materials, medicine, etc. Moreover, the pyramidal compounds are very promising on their own, as the metal-rich clusters that could serve as thermal or photochemical precursors for ceramic composites and nanomaterials (nanoparticles, nanocrystals, nanowires).

Our current study is totally original with no precedents in the proposed experimental strategy, being significant, highly competitive and challenging in the international research arena.

３．研究の方法

(1) In the first step of the project, we will challenge the synthesis of all-group 14 element-pyramidanes by the straightforward reaction of the cyclobutadiene, tetrasilacyclobutadiene, and tetragermacyclobutadiene dianion derivatives with the readily available dichlorogermylene, dichlorostannylene and dichloroplumbylene and their dioxane complexes. Based on our preliminary theoretical studies, such reactions should proceed through the formation of the "housene"-type intermediate, which immediately rearranges into more stable final product, pyramidane.

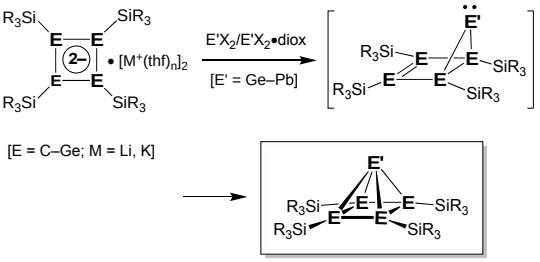
(2) In the next step, we plan to expand the range of accessible pyramidanes by the reaction of the cyclobutadiene dianion derivatives with the group 15 or group 13 element halides to generate the cationic or anionic pyramidanes, respectively, with the heteroatom at the apex of the square pyramid. Then we will optimize the reaction conditions for preparation of all pyramidanes to maximize their yields. Particular attention will be paid for

the right choice of solvent (polar or nonpolar), and the right choice of the main group element halides (fluorides, chlorides, bromides, or iodides).

(3) Following the preparation of pyramidal compounds of the main group elements, we will then systematically study their physico-chemical properties and reactivity. In particular, the non-classical bonding situation in pyramidanes will be studied by means of both experimental methods (X-ray crystallography, NMR spectroscopy, Mössbauer and Raman spectroscopy) and computational approaches (MO analysis, NBP/NPA, topological analysis (ELF, AIM)). The reactivity of pyramidanes towards their practical synthetic application will be also thoroughly explored, for example, their transmetalation reaction with coordination compounds as a route for the synthesis of novel transition metal complexes. **As the potential material science application of pyramidanes, we will study their use as the precursors for ceramic and nanomaterial composites.**

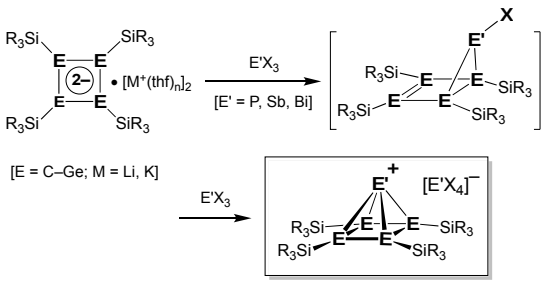
4．研究成果

(1) By the reaction of the cyclobutadiene, tetrasilacyclobutadiene, and tetragermacyclobutadiene dianion dialkali metal salts with the dichlorogermylene, dichlorostannylene and dichloroplumbylene (or their dioxane complexes) we successfully prepared the first examples of the neutral pyramidal compounds entirely consisting of the group 14 elements. All isolated compounds were fully characterized by means of X-ray diffraction, NMR spectroscopy and computational analysis to reveal the non-classical nature of their exceptionally long apex-to-base bonds (**Scheme 2**) [(a) *J. Am. Chem. Soc.* **2013**, *135*, 8794: highlighted in the *C&E News (ACS)*, **2013**, *91*, issue 23, page 28; (b) *Angew. Chem. Int. Ed.* **2015**, *54*, 5654; (c) *Organometallics* **2016**, *35*, 346: highlighted as the *ACS Editor's Choice*].



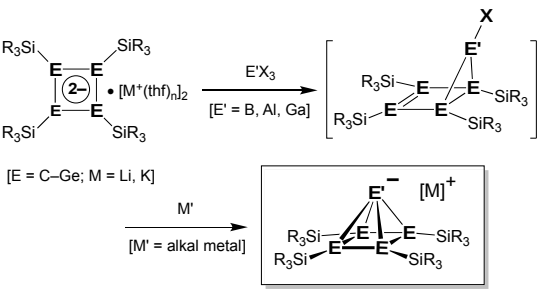
Scheme 2

(2) Expanding the range of the synthetically accessible pyramidanes, we then prepared a series of the cationic pyramidanes with the heavier group 15 element at the top of the square pyramid. Such compounds, which are isoelectronic to the neutral pyramidanes of the heavier group 14 elements, were uniformly prepared by the reaction of the cyclobutadiene dianion derivatives with the group 15 element trihalides $E'X_3$ (Scheme 3). The influence of the reaction conditions (solvent (coordinating or non-coordinating), nature of the halogen X, nature of the heavier group 15 element E′) were carefully investigated to understand the general trends in the stability of the resulting pyramidal systems.



Scheme 3

(2) **Finally, we attempted the synthesis of the anionic pyramidanes with the group 13 elements at the top of the square pyramid. These compounds are isoelectronic to the** neutral pyramidanes of the heavier group 14 elements and also to the cationic pyramidanes of the heavier group 15 elements. We applied the same synthetic approach, namely, the reaction of the cyclobutadiene dianion derivatives with the group 13 element trihalides $E'X_3$, followed by the reduction of the intermediate housenes with alkali metals to generate anionic pyramidanes (Scheme 4). Our preliminary results indicate that the target pyramidanes with the apical boron atom could be prepared, and we will then continue this research aiming isolation of the anionic borapyramidane derivatives, as well as synthesis of pyramidanes with other heavier group 13 elements at the top.



Scheme 4

５．主な発表論文等
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〔**図書**〕（計 3 **件**）

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〔産業財産権〕
○出願状況（計 0 件）
○取得状況（計 0 件）

〔その他〕

６．研究組織
(1)研究代表者
リー　ヴラヂイミール（LEE VLADIMIR）
筑波大学・数理物質系・講師
研究者番号：90375410